Improvement of the Ultra-Trace Voltammetric Determination of Rh in Environmental Samples Using Signal Transformation

C .Almécija[1*], A. Cobelo-García[1] and J. Santos-Echeandía[1]

[1] Grupo Bioxeoquímica Mariña, Instituto de Investigacións Mariñas-CSIC, Vigo, Spain

(*) Corresponding Author: e-mail: calmecija@iim.csic.es

Abstract

Rhodium (Rh) is present at the Earth's surface at ultra-trace concentrations (0.06 ng g^{-1}); however, its use in catalytic converters has increased its deposition nearby traffic pressure and therefore the interest in analytical techniques for Rh determination has increased in the recent years. In this study we propose an improvement of Rh measurement by adsorptive voltammetry applying second-derivative signal transformation.

The optimization of experimental parameters affecting the voltammetric analysis were carried out using sediment samples; these include the amount of sample digest used, the hydrocholoric and formaldehyde concentrations, equilibration time and deposition potential. The use of the second derivative transformation provides well-defined peaks due to the minimization of background interferences, and leads to a significant decrease in the detection limits. Accordingly, a detection limit of 200 fM Rh in the cell was obtained, which corresponds to 14 pg g^{-1} of Rh for 200 mg of sediments.

The optimized methodology was applied to the analysis of Rh in a sediment core collected close to a motorway bridge from Tagus Estuary (Lisbon, Portugal). Here, Rh concentrations ranged from 0.06 to 0.47 ng g^{-1}, showing a surface Rh-enrichment linked to traffic, which is consistent with a Pt superficial peak. Reference materials have been also analyzed, including road dust (BCR-723) and river sediment (JSD-2), and values obtained are in agreement with certified concentrations and previously values reported in the literature.

Key words

Rhodium determination, adsorptive voltammetry, second derivative transformation, sediments

INTRODUCTION

Rhodium (Rh) belongs to the Platinum Group Elements (PGE) – together with platinum (Pt), iridium (Ir), osmium (Os), palladium (Pd) and ruthenium (Ru). As highly siderophile elements, the Earth's core sequesters about 99.8% of PGE [1] explaining their ultra-trace concentrations at the Earth's surface (<1 ng g^{-1}); accordingly, typical Rh concentration in the upper continental crust is 0.06 ng g^{-1} [2]. The use of several PGE – especially Pt, Pd and Rh – as active components in the catalytic converters of motor vehicles, which were developed to transform exhaust emissions (CO, NO_x or CO_2) into more harmless products [3], has increased their environmental concentrations close to traffic pressure [4,5]; also, evidence for a global environmental perturbation has been given from samples collected in remote environments [6,7]. Actually, in 2012 the world demand of Rh for catalytic converters was about 69% of its total demand (~14 tons) [8].

Rhodium is still a challenging element from an analytical perspective due to its ultra-trace concentrations in the environment even at anthropogenically-impacted areas. Several previous works have applied and improved different techniques for Rh determination, including atomic absorption spectrometry [9,10] or neutron activation analysis [11,12]; however, inductive coupled plasma mass spectrometry ICP-MS [13–17] and adsorptive voltammetry [18–26] have become the most widely used method due to their higher sensitivity. Besides, some other studies have solved important issues (e.g. storage problems) [27]. ICP-MS is characterized by rapidity, simplicity and multi-elementary capacity [14–17], although isobaric interferences on Rh^{103} −like $^{63}Cu^{40}Ar^{+}$ or $^{91}Zr^{12}C^{+}$− may cause severe inaccuracies in the Rh quantification [19], more noteworthy at the ultra-trace concentrations of biological or environmental samples. Thus, the removal of interferences (e.g. cationic exchange resins) is essential [15,27]; isotope dilution, usually performed to solve this drawback [15], is not suitable for monoisotopic elements like Rh. In this scenario, several studies [19–21,23–25,28–30] have showed that adsorptive voltammetry is a suitable alternative for Rh determination, due to high accuracy, precision, selectivity and sensitivity as well as low detection limits and economical cost [31].

However, voltammetry presents also some difficulties and limitations for Rh determination related to the complexity of natural matrices and low natural concentrations. Model lab-made samples are easily quantified [28,31], but environmental samples containing complicated matrices may cause severe interferences in the background baseline current (e.g. Zn-peak potential is similar to Rh-peak [19] resulting a ill-defined peak [26]). Moreover, whereas determinations of Rh using voltammetry for biological tissues [19,20,23] or anthropogenically-impacted road dust have been reported [20], the absence of Rh determination in sediments or waters is a constant due to the high detection limits compared to natural concentrations [24,29,30].

Consequently, revising the method for Rh determination by voltammetry is necessary to improve their applicability and efficiency, one of the main challenges in the geochemistry of new emergent ultra-trace contaminants. Therefore, in this study we present an improvement of Rh measurement by adsorptive voltammetry in sediment samples applying the second derivative transformation described as described earlier for Pt [26], leading to a faster method, with lower detection limits, and able to determine natural non-contaminated concentration. Besides, data of Rh concentration in a sediment core collected at a high-traffic area will be presented to reinforce the suitability of the new proposed method.

MATERIAL AND METHODS

Instrumentation and reagents

A Metrohm model 663VA voltammetric stand, equipped with a hanging mercury drop electrode (HMDE) as the working electrode, a $Ag/AgCl/KCl_{sat}$ as the reference electrode and a glassy carbon rod as counter electrode, connected to a μAutolab Type III potentiostat (Metrohm Autoloab B.V.), was used to in the experimental work. The system was controlled by GPES v.4.9 software (EcoChemie B.V.). Samples in the polytetrafluoroethylene (PTFE) voltammetric cell were purged with humidified N_2 (99.9999%; Alphagaz1, Ari Liquide); stirring of the solution was attained using a PTFE rod (speed = 3000 rpm). Mercury used was for analysis and polarography (EMSURE, Merck), and a drop size of 0.52 mm^2 was selected.

Laboratory work was carried out in a laminar flow bench (ISO 5) housed inside an ISO 7 lab where temperature was controlled (25 °C). All the materials used during the experiments were acid pre-cleaned, rinsed with Milli-Q water (Millipore, 18.2 MΩ cm at 25 °C) and handled inside laminar flow hoods.

Reagents used in this study were HNO_3 65% and HCl 30% (Suprapur© Merck), formaldehyde (36.5%, Riedel-de-Haën), H_2SO_4 (≥95%; Trace-SELECT, Fluka) and hydrazine sulfate (Fluka). Solutions of formaldehyde (1.46%) and hydrazine (50 mM) were in Milli-Q water and stored in flourinated ethylene propylene bottles (FEP; Nalgene), being stables during several weeks. Rh and Pt atomic absorption standards (Fluka) were used to prepare weekly working solutions for standard addition.

Rhodium determination in sediment samples

100-250 mg of sediments were ashed in quartz crucibles up to 800 °C (3h) to remove organic matter. Ashed sediments were digested in a mixture of 3 mL concentrated HNO_3 and 5 mL concentrated HCl in 30 mL PFA bombs (Savillex) for 4h at 195 °C using a temperature-controlled Teflon-coated hot plate (PicoTrace). Then, samples were allowed to cool down, caps were removed, and the acid was evaporated until near dryness. Then 1 mL of concentrated HCl was added and evaporated again. Finally, 1 mL of concentrated HCl was added and allowed to redissolve the residue; then Milli-Q water was added and the digest was syringe-filtered using a PFA syringe (Savillex) and 25 mm polyethersulfone membranes with 0.45 μm pore size (Pall) and made up to 25 mL (final HCl concentration ~ 0.38 M) in a polypropylene volumetric flask (Nalgene).

An aliquot of 2 mL of sample is diluted with 8 mL of Milli-Q water and 400μL of HCl (30%) and 200 μL of formaldehyde (1.46%) are added to get the optimized mix to measure in the voltammeter (for reference materials 0.5-1 mL of sample and 9-9.5 mL of Milli-Q water). After 5 minutes of stirring and purging (parameters described in the section above), HMDE is set at -0.7V during 30 s with stirring to promote the Rh (III) adsorption on the mercury drop [19]. After 10 seconds of equilibrium (without stirring) the voltammeter sweeps from to -0.9 to -1.25 V (differential pulse mode) with a time interval of 0.2 s and amplitude interval of 0.025 V. The peak appearing at -1.12 to -1.18 V, at which Rh(III)/Rh(0) reduction takes place, is caused by the catalytically-promoted hydrogen reduction caused by the Rh(0) formed at the surface of the mercury drop. The intensity (A) of this hydrogen reduction (catalyzed by Rh) in the voltammogram is proportional to the Rh concentration in the sample. This Rh concentration is quantified by the method of standard additions.

We have applied to the Rh intensity signal the second derivative signal transformation described earlier [26] in order to improve the sensibility, resolution and detectability of the method. Besides, this methodology enhances the ability of removing the interferences by matrix and other elements. Using GPES v.4.9 software, the original current signal is smoothed, low-pass filter (smoothing factor of 2), to remove the noise whose presence could be amplified after first and second derivative). After smoothing, the second derivative signal transformation is applied and good-shaped-peak- are obtained. The following equation describes the transformation [26]:

$$\frac{dI}{dE}(n) = 0.5\left(\frac{I(n) - I(n-1)}{E(n) - E(n-1)}\right) + 0.5\left(\frac{I(n+1) - I(n)}{E(n+1) - E(n)}\right)$$

were *I (A)* is the current intensity, *E (V)* the applied potential and *n* the data point. The height of the second derivative peak of intensity is recorded as measurement of Rh concentration. The height of the original scan peak also is measured too to compare both methods.

Experiment design

Several variables affecting the sensitivity and accuracy of the Rh determination were optimized. These include: (a) equilibration time needed to reach a constant analytical signal, owing to the well-known slow reaction kinetics of Rh [32]; (b) deposition time; (c) depositional potential; (d) HCl concentration in the cell, and (e) formaldehyde concentration. For carrying out this study a sediment sample has been used in all the experiments to perform the optimization in an environmental real matrix.

Samples

One sediment core was collected in September 2011 in the saltmarsh area of the Tagus Estuary (Lisbon, W Iberian Peninsula), *Samouco Salt Marsh*. Sampling point was located by a 17.2 km long motorway bridge that was open in April 1998, with a daily average of 50000 vehicles [33]. Previous anthropogenic pressure in this area was negligible. Table 1 shows reactive blanks and reference materials (road dust BCR-723 with Rh certified value [34] and stream sediment JSD-2 [35]) used to check the accuracy and precision of the method.

Platinum determination

Platinum was determined in sediments and reference materials as an auxiliary parameter for Rh analysis. Briefly, 150 mg of sediment samples were ashed at 800 °C for 3h to remove the organic matter and digested by a mixture of HCl (5 mL) and HNO_3 (3 mL) using a hot plate at 195 °C (4 h). After complete acid evaporation, 1 mL of HCl and 1 mL of H_2SO_4 were added to re-dissolve the residue and evaporated until no gases were released. Finally, the sediment sample is diluted in 0.1 M HCl, filtered and made up to 25 mL (section 2.2). For voltammetric determination of Pt by the method of standard additions and second derivative transformation [26], 2-4 mL of samples and Milli-Q water up to 10 mL, 65 µL of formaldehyde (1.46%) and 100 µL of hydrazine sulfate (50mM) were added in the cell. After purging and stirring, the deposition at -0.3 V was carried out and the sample was scanned from -0.5 to -1.1 V to measure the Pt peak [26]. For reference materials, the samples digested for Rh were used, adding 300µL of H_2SO_4 directly in the voltammetric.

RESULTS AND DISCUSSION

Second derivative transformation

Figure 1 shows the improvement in peak identification and resolution using the second derivative signal (A/V^2) in for the reference materials BCR-723 (road dust) and JSd-2 (river sediment). For the road dust sample, a shoulder-shaped peak is observed in the original voltammogram using the conditions detailed in Figure 1. The situation is however more complicated in the river sediment sample due to the lower Rh concentration (around 3 ng g^{-1} compared to 12.8 ng g^{-1} in the road dust) and a higher background current, resulting in an undetectable Rh signal in the original scan. The use of the second derivative transformation eliminates the background interference and a clear, well-defined quantifiable peak [26] is observed in both samples increasing proportionally with the successive standard additions.

Optimization of Experimental Parameters

200 mg of the sediment sample from 2-4 cm of the core (Rh concentration ~ 0.3 ng g^{-1}) were digested and used to optimize Rh analysis by voltammetry, in a final solution of ~ 6 ng L^{-1} (2 mL of the sample + 8 mL of Milli-Q water + 30 µL of Rh-spike). Figure 2 and Figure 3 plot each optimization step.

3.2.1 Equilibration time

Due to the well-known slow reaction kinetics of Rh [32], the second derivative voltammetric signal was monitored over a period of more than 2 hours of equilibration time under stirring conditions (Figure 2a). It is shown that at least 30 min are required to reach a plateau in the signal for the sample, whereas the peak potential shifts to more negative values. The situation is different after Rh spikes: here, 5 min equilibration time is enough to get a constant signal.

3.2.2 Deposition potential and accumulation time

The dependence of the height of the Rh peak with the accumulation time was checked up to 120 seconds and it was found to increase linearly (Figure 2b), whereas the peak potential shifted to more negative values at higher accumulation periods. On the other hand, the highest sensitivity was obtained at deposition potentials from -0.5 to -0.9 V; a value of -0.7V was chosen for all subsequent determinations (Figure 2c).

3.2.3 Hydrochloric acid and formaldehyde concentrations

Hydrochloric acid is the optimum supporting electrolyte for the voltammetric determination of Rh [19]. Figure 3a shows that sensitivity increases with the acid concentration in the cell until reaching a plateau at about 0.35M HCl; an optimized HCl concentration of 0.40-0.45M was chosen for the determinations. Similarly, a concentration at 0.022 M of formaldehyde (Figure 3b) was selected. The increase in HCl concentrations had no clear impact on Rh peak potential, whereas for formaldehyde the peak is shifted to more negative values at higher concentrations.

From these results, the best conditions to analyze Rh in natural sediment samples are the following: (i) mixture of 2 mL of digested sample, 8mL of Milli-Q Water, HCl (30%, Suprapur© Merck) at a concentrations of 0.43 M (adding 400 µL of HCl), 200 µL of formaldehyde (1.46%) to obtain a concentration of 0.022M; (ii) after 30 minutes of stirred equilibration, analyze the sample after 300 s of purging, 30 s of deposition at -0.7 V; (iii) sweeping from -0.9 to -1.25 V and (iv) second derivative transformation.

Accuracy, Precision and Detection Limits

Selection of the type of baseline in the second derivative voltammograms is critical for the accuracy of the determination [26]. Accordingly, Figure 4 shows the second derivative voltammogram for a BCR-723 (road dust; certified Rh concentration of 12.8 ± 1.3 ng g^{-1}, Table

1) digest and three different baselines checked: (a) front-peak horizontal baseline, (b) peak-peak baseline and (c) rear-peak horizontal baseline. Using the method of standard additions, concentrations of 8.1, 12.1 and 14.8 ng g^{-1} were obtained by the different baseline methods (a, b and c, respectively); therefore, the peak-peak baseline was chosen for our determination since it provided the most accurate results. Analysis of three separate BCR-723 digests yielded an average Rh concentration of 12.9 ± 1.7 ng g^{-1} (Table 1), indicating a complete recovery, and a relative standard deviation (%) of 13%. For the river sediment reference material (JSD-2) a concentration of 2.9 ± 0.8 ng g^{-1} was found (relative standard deviation 28%); this reference material lacks certified Rh concentration, but the value found here is in agreement with those previously reported by Hall and Oates (2003; [36]; 3.2 ± 1.0 ng g^{-1}) and the one obtained in our lab using ICP-MS for determination (Almécija et al. (in revision) [37]; Table 1).

Procedural blanks resulted in an average Rh concentration in the diluted digest in the voltammetric cell of 180 ± 8 fM ($\bar{x} \pm SD$, $n=6$) which corresponds to a 12 ± 0.5 pg g^{-1} for a typical sediment mass of 200 mg. Detection limit of 200 fM (14 pg g^{-1} for 200 mg of sediment), calculated as $blank + 3 \times SD$ of blanks is satisfactory for the analysis of Rh in uncontaminated sediments and soils (Table 1).

Several previous studies had reported optimal conditions to analyze Rh by adsorptive cathodic stripping voltammetry in natural samples [19,20,23–25]. León [19] developed a method for the simultaneous detection and quantification of Pt and Rh. The detection limit for Leon´s study, 54 fM, is 4 times lower than our detection limit (200 fM; Table 1). However, these values of detection limit are non-comparable: Leon´s detection limit was calculated as $3 \times SD$ of the blank, while the one obtained using our procedure was calculated as $blank + 3 \times SD$ of blanks (180 + 23 fM). Also, Helmers and Mergel´s method [20], similar to ours in electrolytes concentration and deposition potential, needs a 4 times longer deposition time although their samples contain up to 160-fold higher Rh concentration. Besides, the detection limit reported is almost 650-fold our detection limit (1.5 10^4 fM, Table 1). Other authors [23–25] reported other modifications in the method, but not suitable for analyzing real natural concentrations due to too high detection limits.

Application of the Method to Sediment Samples

Figure 5 shows the Rh and Pt profiles in a salt marsh sediment core in the Tagus Estuary. Concentrations ranged from 0.06 to 0.47 ng g^{-1} and 0.58-40 ng g^{-1} for Rh and Pt, respectively. Both elements displayed maximum values at surface decreasing with depth where they reach concentrations similar to their crustal abundance, i.e. 0.06 ng g^{-1} for Rh [2] and 0.51 ng g^{-1} for Pt [38]. The Pt/Rh ratios in the core were 8.7 ± 3.9, similar to crustal values (8.5; Figure 5), with the exception of the surface sample (0-2 cm; Pt/Rh: 85).

The sample point in the salt marsh is located by a high-traffic motorway bridge with a daily average of 50000 cars [33]; the observed surface enrichment linked to the use of Pt and Rh as active components of catalytic converters of motor vehicles has been extensively reported for diverse environmental compartments [4–7] but also in the study area [39,40]. It is however surprising the elevated Pt/Rh (85) obtained for the most recent sediment layer, considering that typical Pt/Rh ratios in catalytic converters is around 5 [41] and that other studies in traffic-impacted compartments also reported lower values (5-16; [4,5,42–45] including the road dust reference material BCR-723 [34]. In spite of this difference in the Pt/Rh ratio, our surface Rh value is in the range of contaminated sediment [43,46].

An important remarkable goal of this study is the almost complete lack of Rh data -analyzed by voltammetry- for sediment samples. Although several authors used sediments, soils or dust to check their methods [24,29] only Helmers and Mergel (1998) [20] reported real Rh concentrations (9.7 and 75.1 ng g^{-1} in road dust), being this concentration 21 to 1300 times higher than our samples. This fact reinforces the idea of the challenge accepted and achieved by our analysis, able to measure contaminated but also no contaminated sediments (Rh concentration less than 0.1 ng g^{-1}), due to the improvement in the determination using second derivative signal transformation.

CONCLUSIONS

In this study we propose a new methodology to analyzed rhodium by catalytic adsorptive cathodic stripping voltammetry applying the second derivative transformation described by Cobelo-García *et al* [26] in a previous study. The higher rapidity in the analysis and the increase in sensitivity – due to minimization of baseline effects – improve the capability of the determination of Rh in natural samples. Besides, the analysis of sediments allows us to measure Rh in contaminated but also non-contaminated samples with natural background concentrations. Therefore, this study supports the second derivative method as a noteworthy alternative for Rh analysis, compatible with complementary analysis (like Pt) in the same decomposition procedure.

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Figure 1: Original and second derivative voltammograms in road dust reference material (left, BCR-723) and river sediment (right, JSd-2) with several standard additions. Conditions: (i) BCR-723: 1 mL of sample digest + 9 mL of MQ-water, initial Rh concentration ~37 pM, and +26.7 pM Rh spiked for each addition; JSd-2: 0.5 mL of sample digest + 9.5 mL of MQ-water, initial Rh concenetration ~ 8 pM, and + 4.5 pM Rh spiked for each addition; (ii) 0.42 M HCl; (iii) 0.022 M formaldehyde, (iv) 30s deposition time, (v) -0.7 V deposition potential.

Figure 2: Variation of sensitivity of the second derivative peak (A/V2 x 10 -3, left column) and peak potential (V, right column) with the optimization of the different parameters: a) homogenization time (min); b) deposition time (s); c) deposition potential (V). For each experiment the other parameters remain invariable: homogenization time = 30 minutes; deposition time 30s; deposition potential -0.7 V; [HCl]= 0.43 M; [formaldehyde]= 0.022 M. (Rh concentration in sample 2-4 cm ~ 0.3 ng g^{-1} and in the cell ~ 6 ng L^{-1}).

Figure 3: Variation of sensitivity of the second derivative peak (A/V^2 x 10^{-3}, left column) and peak potential (V, right column) with the optimization of the different parameters: a) HCl concentration in the cell (mol L^{-1}) and b) Formaldehyde concentration in the cell (mol L^{-1}). For each experiment the other parameters remain invariable: homogenization time = 30 minutes; deposition time 30s; deposition potential -0.7 V; [HCl]= 0.43 M; [formaldehyde]= 0.022 M. (Rh concentration in sample 2-4 cm ~ 0.3 ng g^{-1} and in the cell ~ 6 ng L^{-1}).

Figure 4: Second derivative voltammogram of road dust reference material were three different modes of baseline trace are shown: a) front-peak horizontal baseline, b) peak-peak baseline and c) rear-peak horizontal baseline. Final concentrations in dust calculated were 8.1, 12.1 and 14.8 ng g^{-1} respectively.

Figure 5: Rh and Pt profiles and the Pt/Rh from a sedimentary core at a salt marsh under high traffic pressure of the Tagus Estuary.

Table

Table 1: Rh concentration in refecence materials (Road dust BCR 723 [34] and river sediment JSD-2 [35]) blanks and detection limits (3 SD blank) in this study and other reports (certified cards and other authors´ studies [19,20,23,36,37]).

		Concentration (ng g^{-1})	Concentration in cell (fM)
BCR-723	certified value	12.8 ± 1.3	-
	this study (*n=3*)	12.9 ± 1.7	-
JSD-2	Hall and Oates, 2003	3.18 ± 1.04	-
	Almécija et al.,	2.6 ± 0.2	-
	this study (*n=3*)	2.91 ± 0.80	-
blank (*n=6*)	Sample	12 ± 0.5 (pg g-^{1})*	180 ± 8
detection limit	Sample	14 (pg g^{-1})*	200
	León 1997	-	54
	Helmers and Mergel, 1998	-	1.5 10^{4}
	Orecchio and Amorello, 2010	120 (pg g-^{1})*	-

Values: mean value ± SD
*Values calculated for 200 g of sample

Figure

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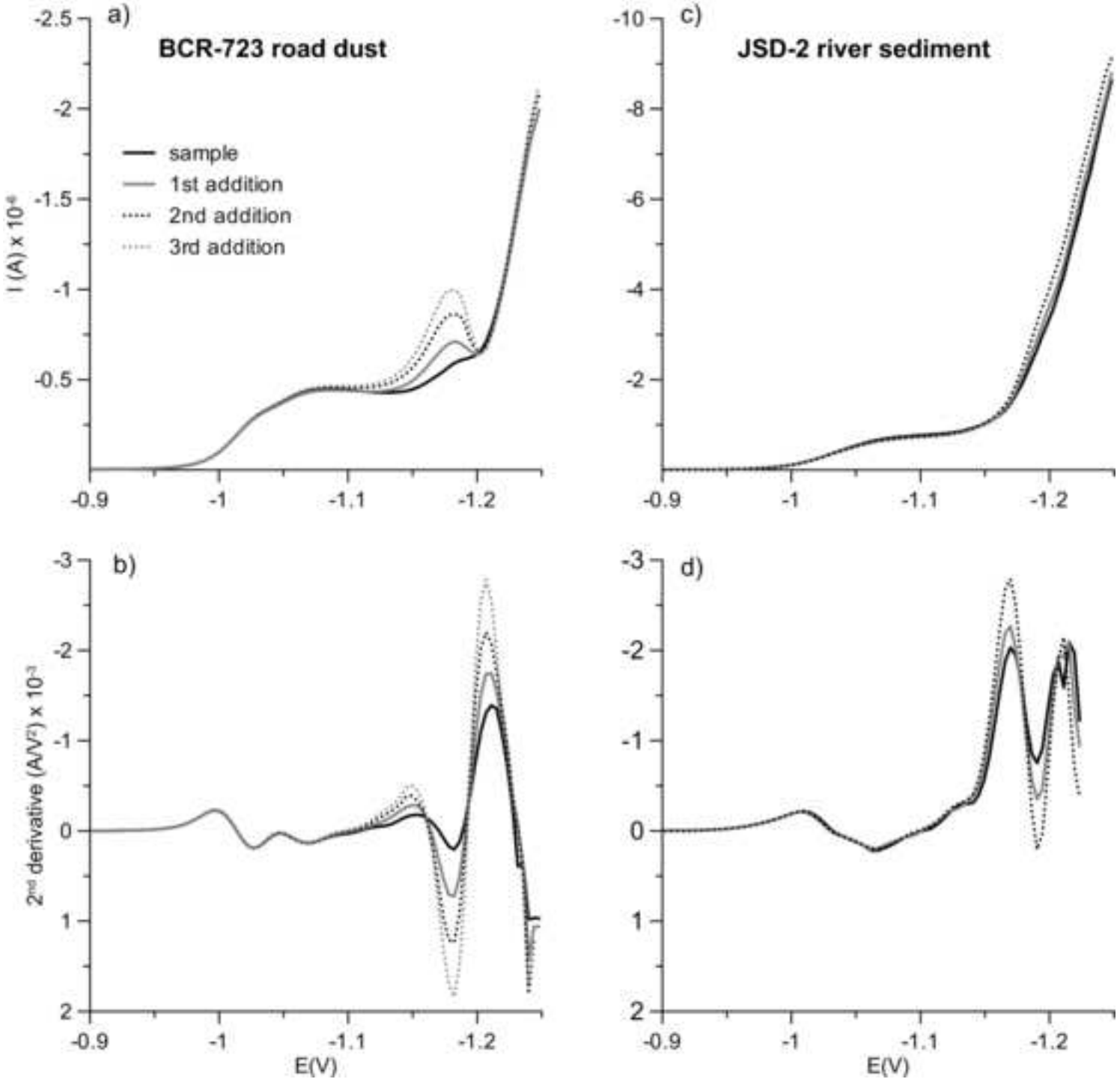

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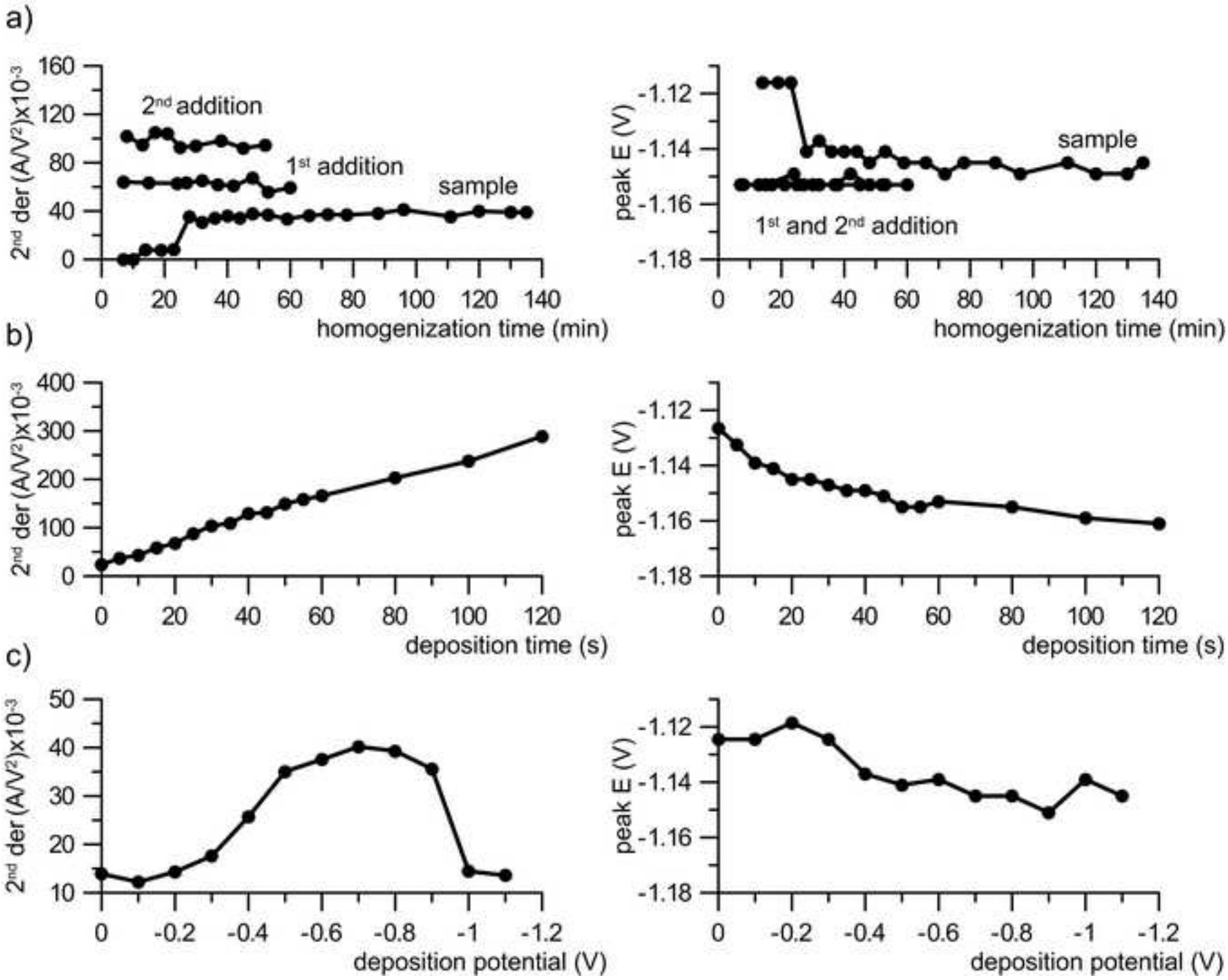

Figure
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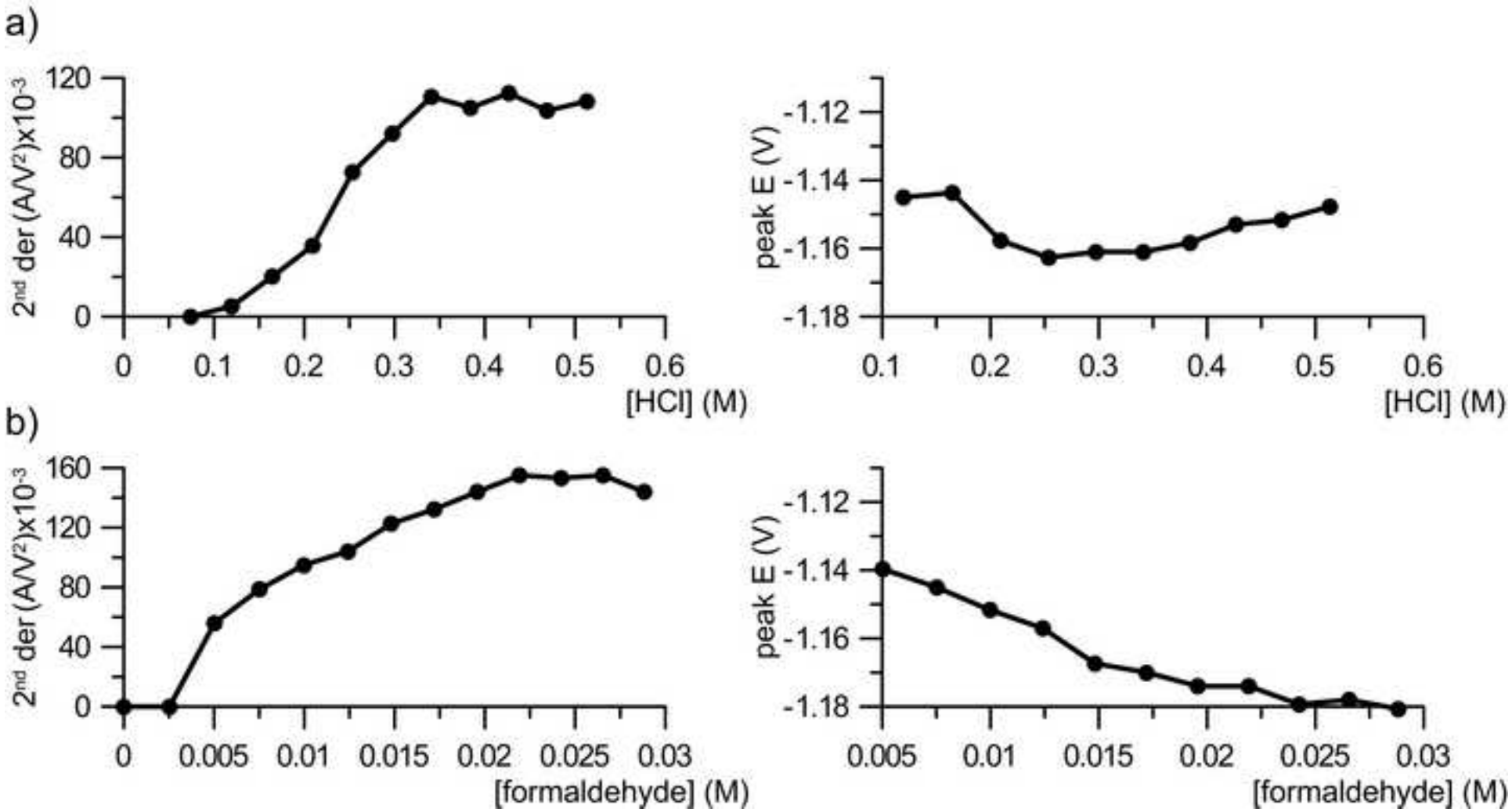

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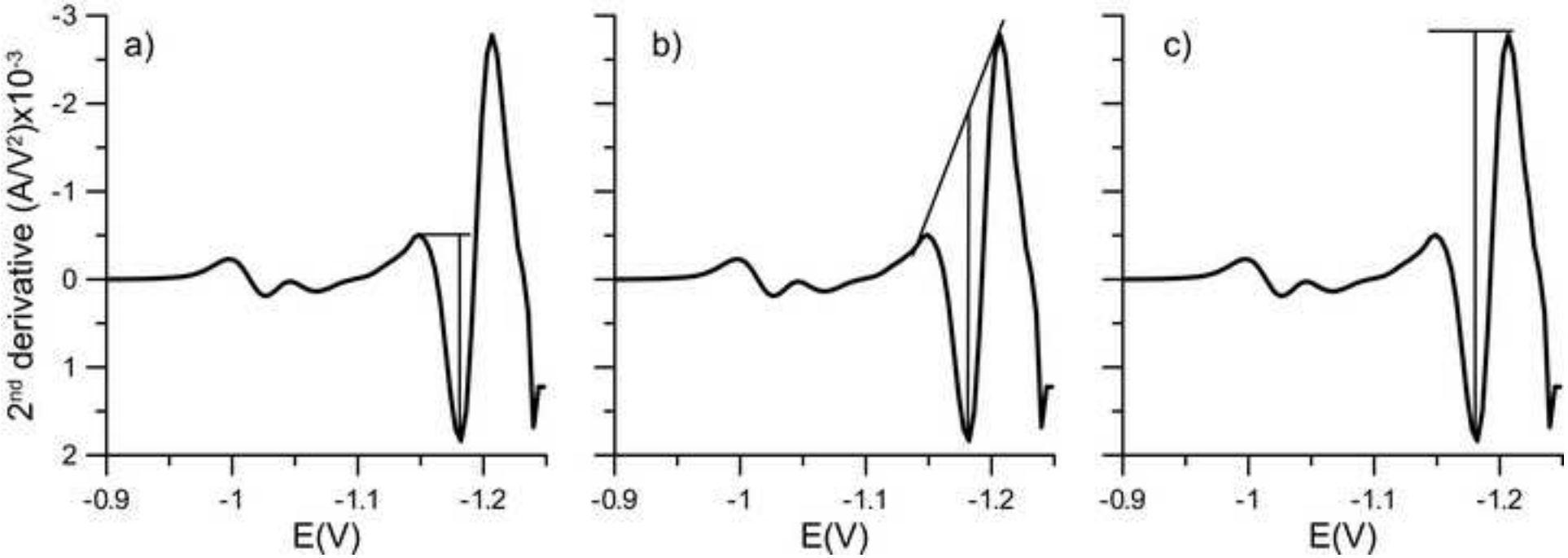

Figure

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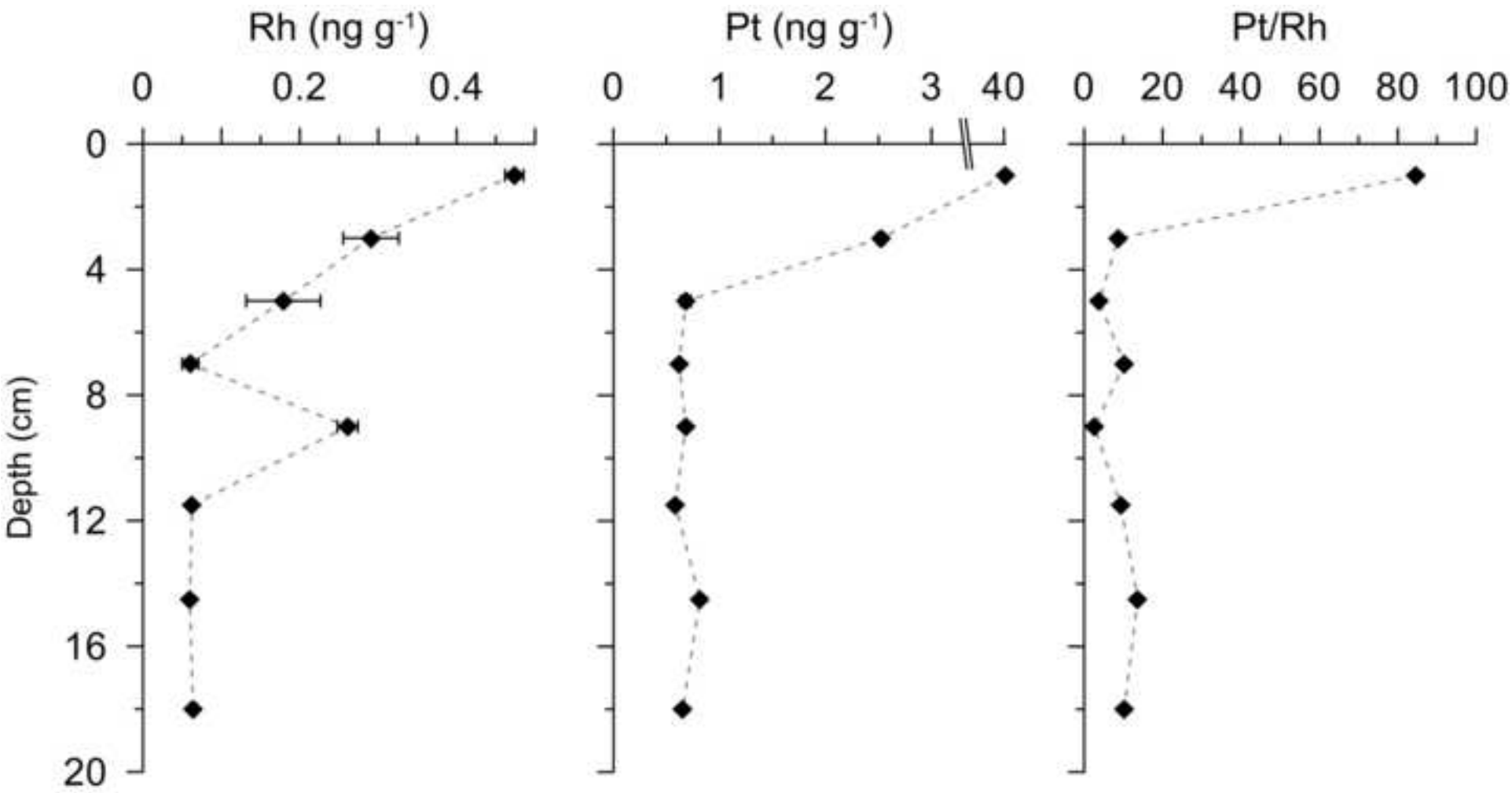

*Graphical Abstract (for review)

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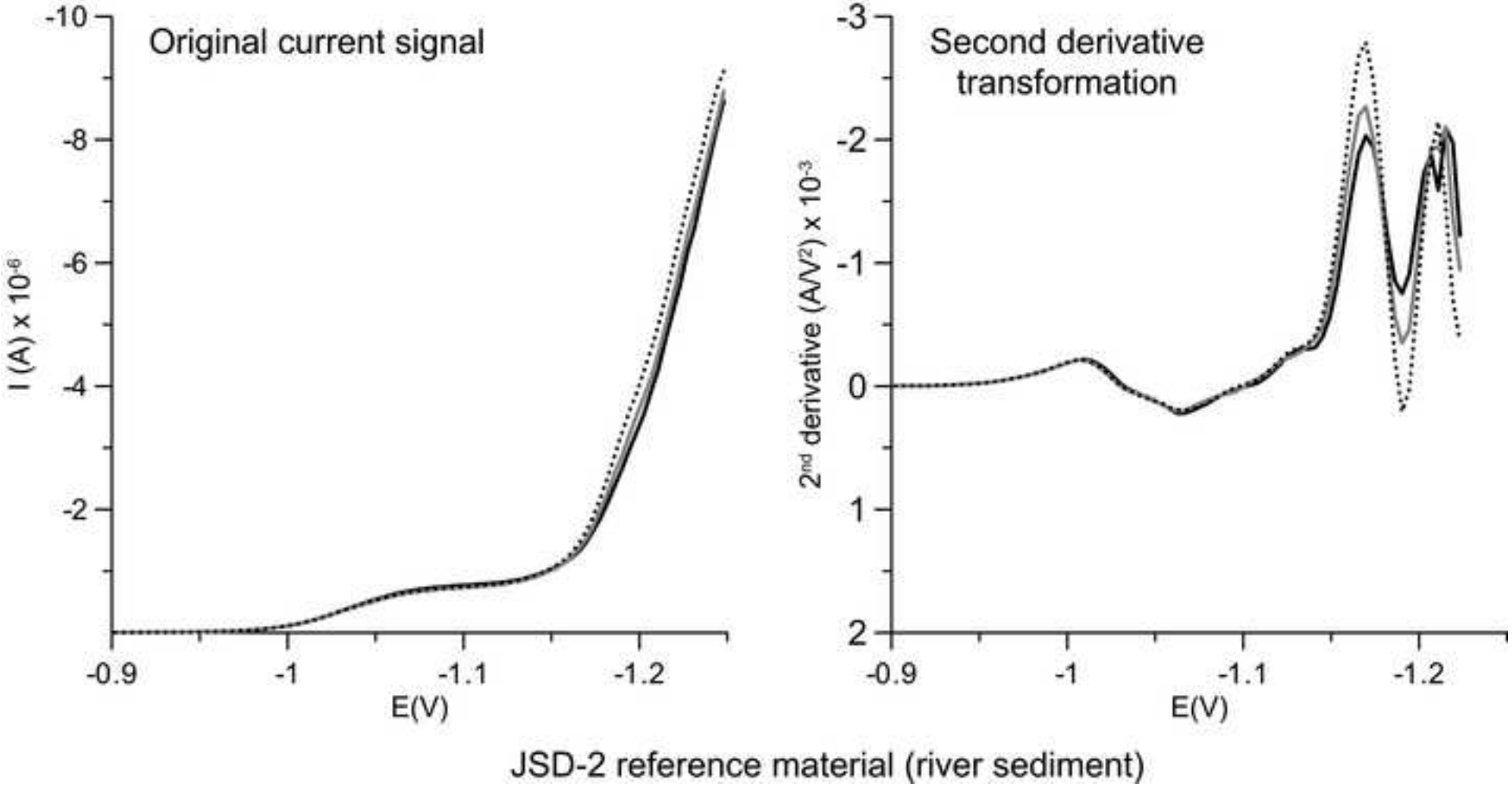

JSD-2 reference material (river sediment)